

Anonymous Referee #1

Received and published: 14 October 2015

This manuscript reports year-long measurements of non-refractory submicron particles by Aerodyne Aerosol Chemical Speciation (ACSM) at an urban (JST) and rural (LRK) sites in the southeastern US. Source apportionments of organic material were made for each season at each site. Overall, this paper is well written and addresses a relevant topic within the scope of the journal. The authors should provide details about how the PMF solutions are determined as well as the uncertainty analysis. I disagree with some of the factor identification and suggest the authors to re-check their analysis carefully. I recommend this manuscript be published after the following comments are addressed.

Specific comments:

(1) Page 22385, line 17-21: *Perma Pure PD-50T isn't designed for flows containing particles. Have the authors tested the particle loss through the dryer?*

We did not test the Nafion dryer ourselves. Aerodyne tested Perma Pure PD-200T (more tubes than 50T model) and found particle losses was less than 10%. ACSM setup requires a high sampling flow rate (3 L/min), which cannot to be achieved using the MD series. Therefore, the PD series was used in the ACSM sampling setup.

(2) Page 22385 to 22386: *The slope obtained from ACSM NR-PM₁ + BC and SEMS PM₁ is complicated with the CE value. Although a CE value of 0.5 was chosen, substantial differences exist when comparing the ACSM results with other measurements at the sites studied herein (Budisulistiorini et al., 2014). Given the large uncertainty of CE (as well as other uncertainties in the ACSM quantification of mass concentration), I don't think it is meaningful to derive the particle density by this method. Also, the authors estimated the particle density based on average composition. It is perhaps better to use 1.4 instead of 1.2 g cm⁻³ for organic material based on our current understanding (Hallquist et al., 2009; Kuwata et al., 2012). Nevertheless, to me, 1.48 in Table S3 and 1.75 for summer JST are quite different. The question is what is the reasonable tolerance for density estimates.*

We agree that the derived particle densities are not very useful for discussion in this study. As a result, we removed this part from the paragraph.

The estimation of dry densities was done to examine if CE of 0.5 was yielding reasonable total submicron aerosol density. For the estimation of particle density, we calculated again using density of 1.4 g/cm³ for organic and updated the table.

We revised the sentences as follow:

“We estimated dry density of ambient PM₁ based on average particle composition for each season, and the assumption of organic, inorganic, and EC densities are 1.4 (Hallquist et al., 2009), 1.77 (Turpin and Lim, 2001), and 1.77 g cm⁻³ (Park et al., 2004), respectively. The estimated dry aerosol densities at both the JST and LRK sites are 1.55 g cm⁻³ on average (Table S3), which is about 10–20% from density of 1.75 at JST (Budisulistiorini et al., 2014) and 1.52 g cm⁻³ at LRK (Budisulistiorini et al., 2015) during summer at LRK. If a CE of 1 was applied to JST and LRK datasets, the estimated aerosol density is <1 g cm⁻³, which is much lower than the suggested organic aerosol density of 1.4 g cm⁻³ (Hallquist et al., 2009) and inorganic aerosol density of 1.77 g cm⁻³ (Cross et al., 2007). Therefore, we applied a CE value of 0.5 on all seasonal datasets.”

(3) Page 22386, last paragraph: *The determination of the “best” PMF solution for each case*

seems quite subjective. Although Figures S2-S9 are provided for the PMF diagnostics, there is no description about them. It was mentioned that the uncertainties of selected solutions were investigated with the seed, fpeak, and bootstrapping tests. But I can't find any further information. The authors should provide the details about the best-solution determination and the uncertainty analysis. Some questions regarding the PMF diagnostics are listed below.

- The Q/Q_{exp} values are not near 1, and are different for the JST (2-3) and the LRK (~0.2) best solutions. Have the errors of the input data and the downweighting treated properly? If the Q/Q_{exp} contributions are dominated by a few temporal spikes or plumes, test PMF runs excluding those time periods should be performed and analyzed. It is not unlikely that certain plume events represent source profiles very different from the long-term profiles. The authors should make sure those events won't bias the PMF solutions.

The Q/Q_{exp} values $\gg 1$ in JST PMF analysis suggests that errors were underestimated. We have omitted the temporal spikes in all datasets and downweighted the bad and weak ions. In doing so, JST datasets were left with quite large number of missing datapoints that variability could not be modeled. LRK datasets were treated in similar manner, i.e., omission of temporal spikes and downweighting of bad and weak ions. The low Q/Q_{exp} values in LRK PMF analysis suggest that errors were overestimated. Overall, OA concentration in LRK was lower than JST, and for some periods the concentrations could be less than detection limit of ACSM instrument ($0.3 \mu\text{g}/\text{m}^3$). The low OA at LRK could result in lower signal-to-noise ratio and overestimation in errors.

- Figure S2: It looks like there are significant Q/Q_{exp} contributions from marker ions of m/z 41 to 60. What does the 5 factor solution look like?

The five-factor solution of JST winter 2012 PMF analysis resulted in a split factor, which has SV-OOA and BBOA time series and profiles characteristics. The 5th factor time series is correlated with BBOA and SV-OOA ($R \sim 0.7$). Adding the 5th factor yielded a lower correlation ($R < 0.6$) of BBOA with primary emission tracers (i.e., CO and BC), SV-OOA with NO₃. Moreover, reduction in overall Q/Q_{exp} value is $< 10\%$ for the five-factor solution. Thus, we will keep the four-factor solution for JST winter 2012.

- There are still some patterns in the residual time series for the "best" solutions that need to be checked, for example, March in Fig. S2, April in Fig. S3, earlier October and December in Fig. S5, and mid March in Fig. S6. Those features may indicate that more factors are needed to explain the data. Besides, the season separation may not be ideal and adjustments may be needed.

We have examined adding number of factors for those cases. At each case, additional factor yielded split factor(s) that correlate with other factors time series or mass spectra. The additional factor(s) also show lack of correlation with external gas- and/or particle-phase tracers, which cause difficulties in chemically characterizing the factor(s). We acknowledge that comprehensive collocated particle-phase tracers analysis was unavailable, thus limiting PMF factor analysis.

- The chosen of a particular rotation (e.g., $f_{peak} = -0.15$ for LRK spring in Fig. S7 and -0.1 for LRK fall in Fig. S9) needs to be well explained. It looks like the factor mass spectra are highly correlated for those cases. Tuning rotation to obtain more distinct markers like m/z 82 and 91 would bias the PMF analysis.

When we tuned fpeak, we were checking and making sure the rotation did not significantly change factors mass spectra. The fpeak was selected based on correlation of factors time series to external tracers (e.g., SO₄, NO₃, CO, BC, etc). We have been careful in tuning the mass spectra (positive fpeak) to avoid obtaining more distinct ion markers that would bias the PMF analysis. We added explanation about the selected rotation in the SI section.

- (3) Page 22388, line 22: *It should be clarified in the text or figure caption that some of the data are published in Budisulistiorini et al., 2015.*

We added this information in Method section.

“Organic and inorganic species characterizations during 2013 Southern Oxidant Aerosol Study (SOAS) published in Budisulistiorini et al. (2015) were included in the analysis of the summer season at the LRK site of this study.”

- (4) Page 22389, line 12-14: *How big could the under-prediction be if organosulfates are considered? Studies suggest organosulfates accounted for up to 30% of the organic mass and 4-14% of total sulfate (Lin et al., 2012 and references therein). Have the authors done any analysis on the ambient samples at the sites to quantify the amount of organosulfates?*

We quantified isoprene- and monoterpenes-derived organosulfates using authentic standard of 2-methyltetrols sulfate (m/z 216) and α -pinene sulfate (m/z 250). Quantification of isoprene-derived organosulfates has been published in Budisulistiorini et al. (2015). The isoprene OS accounted ~3.5% and ~9.5% of the OA and sulfate mass measured by ACSM, respectively. In contrast to East Asia findings in Lin et al. (2012), monoterpene OS were very low (0.012 $\mu\text{g}/\text{m}^3$) and no sesquiterpene OS were found at LRK. Aerosol acidity estimation is influenced by concentrations of inorganic aerosol constituents as well as organic water content. We could not estimate contribution of OS to aerosol liquid water content using the available data.

- (5) Page 22391, line 22-30: *The production of SOA may be balanced out by the loss and hence appeared as day-time valley. It looks like all OOA-factors and inorganic species show similar diurnal patterns that decrease during the day. Could the authors show data like the diurnal PBL height and other meteorological parameters to specify the main driver of the day-time decrease? Why do the minimum concentrations of nitrate, organic material, sulfate, and ammonium appear at different time (Fig. 4a)?*

We, unfortunately, did not have LIDAR measurements at JST and LRK, and thus we could not provide PBL height profile. Acknowledgement of the missing PBL height profile has been added to OA characterization section.

“Due to lack of measurements, the potential role of planetary boundary layer (PBL) height to diurnal variation of PMF factors was not accounted for in this study. However, it is acknowledged here that diurnal PBL dynamics or loss processes (e.g. deposition) could influence diurnal patterns observed here for the PMF factors.”

The difference in minimum concentration of inorganic species and organic matter could be influenced by not only PBL height but also different characteristics of each species. Sulfate increased in the afternoon, likely due to increasing photochemistry. Since nitrate is semi-

volatile, it most likely decreases when temperature was higher. Diurnal profiles of ammonium were quite insignificant, except those during winter and fall season. Organic diurnal profiles were highly influenced by sources and atmospheric processing.

- (6) Page 22392, line 19-30: *I would argue that the 91Fac reported in Robinson et al., 2011 (Supplementary) is more likely the HOA factor (see the high R2 values in Table S1). The f43/f44 ratio for the Robinson 91Fac factor (1.2) is also much greater than the ratio herein (0.12). The caveat is that f43/f44 is also sensitive (usually) to the rotation. Overall, I tend to agree with the assignment of this factor at LRK as 91Fac, similar to those identified in Budisulistiorini et al., 2015 and Chen et al., 2015. But at JST spring (summer as well), because the small mass fractions of the 91Fac, noisy temporal variations (Fig. 3a), and the high correlation of the mass spectrum of this factor with LV-OOA. I think it is more likely a “split” factor, which needs to be carefully reanalyzed.*

As pointed out by referee, temporal variation of 91Fac resolved from PMF analysis of JST spring and summer 2012 are noisy. Re-analysis of JST spring and summer 2012 suggested that at least three-factor solution is needed to explain OA from spring and summer datasets. Four factor solution yielded a factor with noisy temporal variation as previously resolved. Five factor solution also yielded factors with noisy temporal variation. In conclusion, three-factor solution was selected as the best fit based on correlation of factors' time series and profiles with external tracers and references, respectively.

- (7) Page 22393, line 7-13: *The 82 marker seems not present in the IEPOX-OA factor here (Fig. 2b). The spectrum is highly correlated with LV-OOA (R2_0.9) but less correlated with lab IEPOX SOA (Tables S1-S2). How confident do the authors believe this is not a “split” factor, or something else (e.g., some type of SV-OOA), but a real IEPOX-OA factor? Similarly for the fall, relatively high 82 and m/z 53 (associated with the 82 peak (Budisulistiorini et al., 2013; Chen et al., 2015; Robinson et al., 2011) are missing (Fig. 2d). The authors should carefully check the PMF analysis for the spring and fall.*

Mass spectrum of 82Fac (Robinson et al., 2011) is correlated ($r^2 = 0.84$) with LV-OOA (Ng et al., 2011). Thus, it is somewhat expected that IEPOX-OA from both JST spring and summer are well correlated ($r^2 \sim 0.9$) with reference LV-OOA (Ng et al., 2011). Correlations of JST spring and summer IEPOX-OA with IEPOX-OA resolved from Atlanta 2011 and SOAS 2013 (Budisulistiorini et al., 2013 and 2015) are very strong ($r^2 \geq 0.9$). Laboratory-generated IEPOX SOA is better correlated with JST spring and summer IEPOX-OA (r^2 0.5-0.6) than with LV-OOA ($r^2 = 0.37$). Thus, we are confident that the IEPOX-OA resolved from JST spring and summer PMF analysis is a real factor associated with IEPOX SOA.

JST fall 2012 PMF analysis did not resolve IEPOX-OA factor, and only at LRK site we resolved IEPOX-OA factor in fall season.

Signal of m/z 82 varied seasonally, which was likely related to isoprene emission variation. At LRK during spring and fall 2013, the m/z 82 signal of IEPOX-OA was much lower than that in summer. This suggests variation in source of IEPOX-OA factor. Ion fragment at m/z 53 (mostly $C_4H_5^+$) was recommended by Lin et al. (2012) to aid in PMF factor identification. However, in this study we found that this ion did not strongly correspond to m/z 82 fragment.

IEPOX-OA from LRK spring and fall 2013 PMF analysis are strongly correlated (r^2 0.8-1.0) with IEPOX-OA from Atlanta 2011 and SOAS 2013 (Budisulistiorini et al., 2013 and 2015).

Laboratory-generated IEPOX SOA is better correlated with LRK fall 2013 IEPOX-OA ($r^2 \sim 0.5$) than with LV-OOA (r^2 0.2-0.3). Thus, we are confident that IEPOX-OA resolved from LRK spring and fall PMF analysis is a real factor.

- (8) *Page 22395, line 1-6: The 91Fac for LRK fall seems being mixed with HOA although f44 is high. The CxHy+ ion series clearly present, and in particular, m/z 57 stands out. For comparison, biogenic-related 91 factors are expected to have a m/z 53-55 pattern (Chen et al., 2015).*

Correlation of LRK fall 2013 91Fac mass spectrum vs. reference HOA is low ($r^2 \sim 0.2$), while correlations with Borneo and SOAS 2013 (Robinson et al., 2011 and Budisulistiorini et al., 2015) are stronger (r^2 0.6 – 0.8). In addition to distinct ion fragment at m/z 91, Robinson et al. (2011) and Budisulistiorini et al., (2015) observed distinct m/z 55 and 57 fragment from 91Fac in forested areas. Chen et al. (2015) observed significant m/z 53 and 55 signals from laboratory experiment with biogenic SOA. We also observed differences between laboratory-generated IEPOX SOA (distinct m/z 82 and 100 fragments, Lin et al., 2012) and field IEPOX-OA factor (distinct m/z 101 fragment than m/z 100, Budisulistiorini et al. 2013, 2015). The differences in mass spectra obtained from laboratory experiments and field observations could be attributed to complex atmospheric processes.

- (9) *Given the differences in the mass spectra and diurnal profiles of one factor for different seasons (Fig.2), PMF analysis for combined datasets of different seasons should be done to test if the results are robust and meaningful.*

We have done PMF analysis of combined datasets. Some factors resolved in separate datasets were not able to be resolved in the combined datasets. Signal of these factor(s) might be low and/or specific to certain period (for example BBOA and biogenic SOA), and have similar characteristics (for example SV-OOA and IEPOX-OA). By combining the datasets, these factors are averaged over long period, and lose their distinct characteristics. This issue might be specific to low-time resolution instruments such as the ACSM.

Technical remarks:

Page 22388, line 26: It is better to specify here as “non-refractory chloride”.

It has been revised as follows:

“Average non-refractory chloride loadings were low ($<0.1 \mu\text{g m}^{-3}$), indicating that it is not a significant contributor to inorganic aerosol mass in this region.”

Page 22393, line 1 and p22399, line 3: “Chen et al., 2014” should be “Chen et al., 2015”.

The reference has been revised.

Figure 2. The signals for ions above m/z 60 are too low to see. Ion markers (e.g., 82 and 91) are difficult to tell. Either additional figures or amplified right axes are needed.

We separated mass spectra from JST and LRK into Fig. 3 and 4, respectively. Thus, the ion signals are now more readable.

Reference:

- Budisulistiorini, S. H., Canagaratna, M. R., Croteau, P. L., Marth, W. J., Baumann, K., Edgerton, E. S., Shaw, S. L., Knipping, E. M., Worsnop, D. R., Jayne, J. T., Gold, A., and Surratt, J. D.: Real-time continuous characterization of secondary organic aerosol derived from isoprene epoxydiols in downtown Atlanta, Georgia, using the Aerodyne aerosol chemical speciation monitor, *Environ. Sci. Technol.*, **47**, 5686-5694, 10.1021/es400023n, 2013.
- Budisulistiorini, S. H., Canagaratna, M. R., Croteau, P. L., Baumann, K., Edgerton, E. S., Kollman, M. S., Ng, N. L., Verma, V., Shaw, S. L., Knipping, E. M., Worsnop, D. R., Jayne, J. T., Weber, R. J., and Surratt, J. D.: Intercomparison of an Aerosol Chemical Speciation Monitor (ACSM) with ambient fine aerosol measurements in downtown Atlanta, Georgia, *Atmospheric Measurement Techniques*, **7**, 1929-1941, 10.5194/amt-7-1929-2014, 2014.
- Chen, Q., Farmer, D. K., Rizzo, L. V., Pauliquevis, T., Kuwata, M., Karl, T. G., Guenther, A., Allan, J. D., Coe, H., Andreae, M. O., Pöschl, U., Jimenez, J. L., Artaxo, P., and Martin, S. T.: Submicron particle mass concentrations and sources in the Amazonian wet season (AMAZE-08), *Atmos. Chem. Phys.*, **15**, 3687-3701, 10.5194/acp-15-3687-2015, 2015.
- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, **9**, 5155-5236, 2009.
- Kuwata, M., Zorn, S. R., and Martin, S. T.: Using elemental ratios to predict the density of organic material composed of carbon, hydrogen, and oxygen, *Environ. Sci. Technol.*, **46**, 787-794, 10.1021/es202525q, 2012.
- Lin, P., Yu, J. Z., Engling, G., and Kalberer, M.: Organosulfates in humic-like substance fraction isolated from aerosols at seven locations in East Asia: a study by Ultra-High-Resolution Mass Spectrometry, *Environ. Sci. Technol.*, **46**, 13118-13127, 10.1021/es303570v, 2012.
- Robinson, N. H., Hamilton, J. F., Allan, J. D., Langford, B., Oram, D. E., Chen, Q., Docherty, K., Farmer, D. K., Jimenez, J. L., Ward, M. W., Hewitt, C. N., Barley, M. H., Jenkin, M. E., Rickard, A. R., Martin, S. T., McFiggans, G., and Coe, H.: Evidence for a significant proportion of secondary organic aerosol from isoprene above a maritime tropical forest, *Atmos. Chem. Phys.*, **11**, 1039-1050, 10.5194/acp-11-1039-2011, 2011.